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THE KINETICS OF THE INITIATING REACTION
AND THE PROPERTIES OF THE INTERMEDIATE CATALYST
IN THE OXIDATION OF PROPANE IN THE PRESENCE OF HBr

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In our previous reports, experimental proof was presented in regard to existence of a new mechanism for homogeneous gas catalysis [1,2]. This mechanism considers the process of catalytic oxidation of a hydrocarbon (propane) in the presence of the homogeneous catalyst HBr as a sequence of two stages, each of which proceeds according to a chain mechanism. The first stage occurs at the very beginning of the reaction, leading to the formation of small amounts of an intermediate catalyst I. The second, slower stage, is a process of induction by the catalyst of the principal chain reaction of oxidation.

Data on the kinetics of the initiating reaction and properties of the intermediate catalyst support our views in regard to the new mechanism of homogeneous catalysis. These data are outlined in the present article.

The data were obtained by using the phenomenon of the critical concentration of acetone, which has been described in a previous report [2]. Acetone, added in sufficient amounts to the initial mixture of propane, oxygen, and HBr, completely suppresses the formation of this chief reaction product [i.e., of acetone]. Adding acetone to the reacting mixture (when the reaction is already under way), after the initiating reaction has been practically completed, has no effect on the kinetics of the reaction nor on the final yield of acetone, even if this substance is added in amounts exceeding the critical.

It is clear that by introducing acetone in critical amounts throughout the course of the initiating reaction and then fixing the final yield of acetone, it is possible to obtain the kinetic rule for the formation of the intermediate catalyst during the course of the initiating reaction.

- 1 -

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Experiments were conducted in the following manner. A mixture of 41.5% propane, 41.5% oxygen, and 17% HBr in constant amounts (i.e., at pressures which decreased correspondingly to decreases in temperature) was introduced into a quartz-glass reaction vessel which had been evacuated to a high vacuum and placed in an oil bath with a definite temperature (170, 150, 130, 110, and 90°) of the oil. At various intervals after the start of the reaction, critical amounts of acetone were blown into the reaction vessel, and the oil bath heating the reaction vessel was exchanged for another with a constant but higher (215°) temperature of the oil. At 215°, the reaction went to completion (the mixture was kept on the bath for no less than 8 min). Thus, the intermediate catalyst formed during the course of the initiating reaction, and up to the moment of adding the critical concentration of acetone, reacted under identical conditions in all cases (the same temperature, equal to 215°, and the same pressure, equal to 100 mm at 215°). Consequently, the final yield of acetone at 215° could serve as a measure of the quantity of intermediate catalyst formed during the course of the initiating reaction at the temperature and during the period in question.

Figure 1 (appended) shows kinetic curves at various temperatures for the formation of the intermediate catalyst during the course of the initiating reaction. The concentration of the intermediate catalyst is expressed in fractions of the concentration that corresponds to the reaction at 215°. It is clearly seen that lowering of the temperature increases the duration of the initiating reaction and decreases the amount of intermediate catalyst formed. There is practically no intermediate catalyst formed at 90° (unshaded) circles on the time axis). Comparing the time which the initiating reaction requires in order to take place with the times for the main reaction of acetone formation (see Figure 1 of source 1 in bibliography), we see that the initiating reaction is much faster than the main process. For example, at 170° the initiating reaction takes a little over a minute, but the process of acetone formation at 168° lasts about 60 min.

The character of the kinetic curves for the formation of acetone draws attention -- these are typical S-shaped curves with a point of bending which corresponds to 50% of conversion. It is known that just this type of kinetic curve is characteristic for branched chain reactions. Thus, the character of the kinetic curves makes our assumption in regard to the mechanism of the initiating reaction highly probable.

The kinetic curves of Figure 1 could be superimposed on one chosen as a standard, if the extent of all of the reactions is adjusted to that of the standard reaction, and the scale of the time axis is changed. The activation energy of the initiating reaction, equal to 13.5 kg-cal/mole, is determined from the magnitudes of the transformation coefficients. It should be noted that the yields of acetone show a stronger drop with decreasing temperatures than the extent of the initiating reaction. This means that as the temperature drops, not only does the amount of intermediate catalyst decrease but also the length of the reaction chain of acetone formation induced by the decomposition of this catalyst.

The relationship between the length of the chain and the temperature can be determined by making use of the phenomenon of the critical concentration of acetone. This phenomenon enables us to prove in an equally simple manner the correctness of our statements concerning the kinetic rule for the decomposition of the intermediate catalyst (one of its properties). For that purpose, the initiating reaction was carried out at 215°, the critical amount of acetone added, and the vessel submerged into an oil bath at 170° and kept there for varying periods. Then, the oil bath was exchanged for a standard one at 215°, the reaction continued to its end, and the amount of supplementarily formed acetone in the mixture determined by deduction of the added critical amount and of the acetone which had formed at 170° (determined in special blank experiments). By returning the mixture anew after various time intervals to 215° and continuing the reaction to its end, we thus determined the amount of intermediate catalyst which did not have time to decompose at 170°, i.e., the kinetic rule for the reaction.

- 2 -

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50X1-HUM

As we already know the rate constant for the formation of acetone, which is identical with the rate constant for the monomolecular reaction of the decomposition of the intermediate catalyst, it is possible to trace the kinetic rule for the decomposition of the intermediate catalyst at 170° and compare the values thus obtained with the experimental results.

Figure 2 (appended) illustrates the extent of congruity of experimental values with theory and decisively confirms our views on the catalysis mechanism.

Unfortunately, lowering the temperature after carrying out the initiating reaction enhances the stability of the intermediate catalyst only up to a certain temperature. Cooling of the reaction mixture to a temperature below 80° leads to a complete and rapid deterioration of the intermediate catalyst, apparently because of a change in its aggregate state.

Thus, it is difficult at present to approach the problem of collecting the intermediate catalyst with the aim of establishing its chemical nature and directly studying its chemical properties.

However, the kinetic method described in the present report permits us to study the kinetics of the initiating reaction and the properties of the intermediate catalyst without separating and identifying it. This makes it possible to initiate a further, more thorough investigation of the new mechanism of homogeneous catalysis.

BIBLIOGRAPHY

1. Z.K. Mayzus, N.M. Emanuel', Dok Akad Nauk, Vol 87, No 2 (1952).
2. Z.K. Mayzus, N.M. Emanuel', Dok Akad Nauk, Vol 87, No 3 (1952).

[Appended figures follow.]

- 3 -

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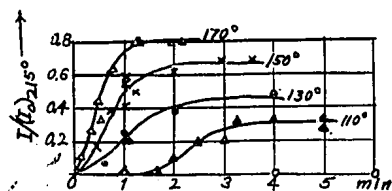


Figure 1. Kinetic curves of the initiating reaction (formation of the intermediate catalyst I) at various temperatures.

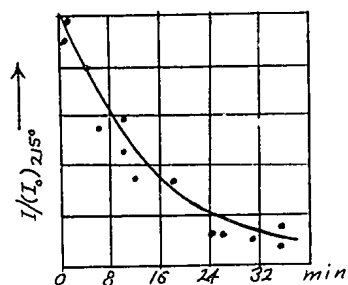


Figure 2. Decomposition rule for the intermediate catalyst I at the temperature of 170° . Curve constructed from the formula:
 $I/(I_0)_{215^\circ} = e^{-kt}$, where $k = 0.07 \text{ min}^{-1}$.
 The dots correspond to experimental data.

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- 4 -

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